

Study of Kinetics of Bromophenol Blue Fading in Alcohol-Water Binary Mixtures by SESMORTAC Model

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Solvent effects on the kinetics of bromophenol blue fading have been investigated within a temperature range in binary mixtures of methanol, ethanol, 1-propanol, ethylene glycol and 1,2-propanediol with water of varying solvent compositions up to 40% by weight of organic solvent component. Correlation of $\log k$ with reciprocal of the dielectric constant was linear. Finally a mechanism was proposed for the bromophenol blue fading upon SESMORTAC (study of effect of solvent mixture on the one-step reaction rates using the transition state theory and cage effect) model, by means of this model, the fundamental rate constants of the fading reaction in these solvent systems were calculated.

Key Words : SESMORTAC model, Kinetics, Alcohol, Bromophenol blue, Binary mixture

Introduction

Bromophenol blue (BPB) is a member of triphenylmethane dyes family.¹⁻³ In alkaline solution it forms a dibasic salt which gradually fades.⁴⁻⁷ In this work, kinetics of alkaline fading of BPB was studied in binary mixtures of methanol, ethanol, 1-propanol, ethylene glycol, and 1,2-propanediol with water over a range of solvent compositions and temperatures. These media provide a useful range of dielectric constant and medium effects.

Experimental Section

Reagent. Ethylene glycol (99%) was supplied by BDH and sodium hydroxide, methanol (99.5%), ethanol (99.8%), 1-propanol (99%), 1,2-propanediol (99.5%) and bromophenol blue were purchased from Merck. Materials were used without further purification.

Procedure. For preparation of dye solution, 0.015 g dye was dissolved in 0.5 cm³ ethanol (99.8%) which after dilution with double distilled water was transformed into a 100 cm³ volumetric flask and was filled to the mark and its concentration was 2.31×10^{-4} mol dm⁻³. The rate of fading was studied by photometric method. A small volume (0.2 cm³) of dye solution was added to 2.5 or 3 cm³ of a solution

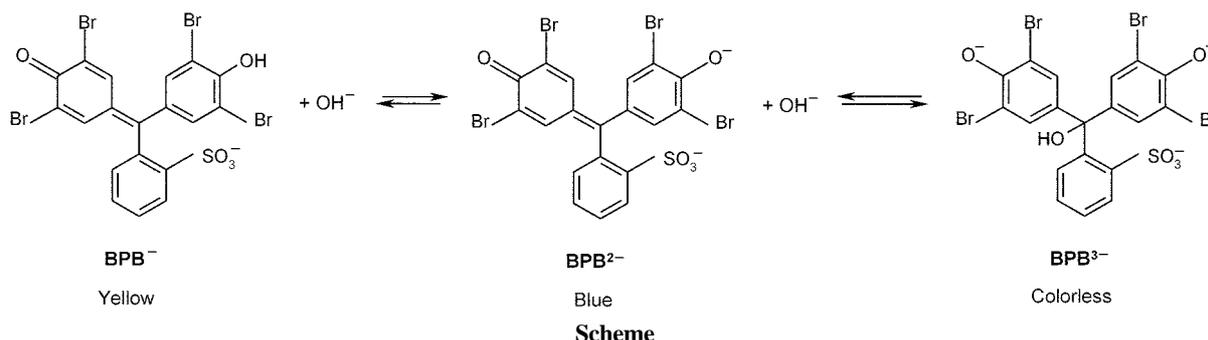
of NaOH (0.2 mol dm⁻³) prepared in alcohol-water mixtures which previously placed in the thermostated cell compartment of a UV-VIS 2100 Shimadzu spectrophotometer (controlled to ± 0.1 °C).

The changes of absorption of dye at its maximum wavelength (λ_{\max}) were recorded at 40-100 minutes intervals. The λ_{\max} values of dye were shifted to red in alcohol-water media, Figure 1.

Theory

Medium effects on reactivity can be very large. A sufficiently drastic change in medium may affect not only kinetic parameters but also rate laws and mechanism and in some cases, reaction products. The rationalization of the important part that the solvent may play in determining reactivity goes back a long way.^{8a}

Chemical reaction mechanisms are discussed in textbooks. But it would be important to say that in rate equations of organic or inorganic reactions which proceed through the formation of activated complex in binary mixtures, there is no term clearly showing the correlation between reaction rate and concentration of solvent components.^{8b,9,10} In cases where none of solvent mixture components are reactant, in a series of experiments in which the concentrations of mixture



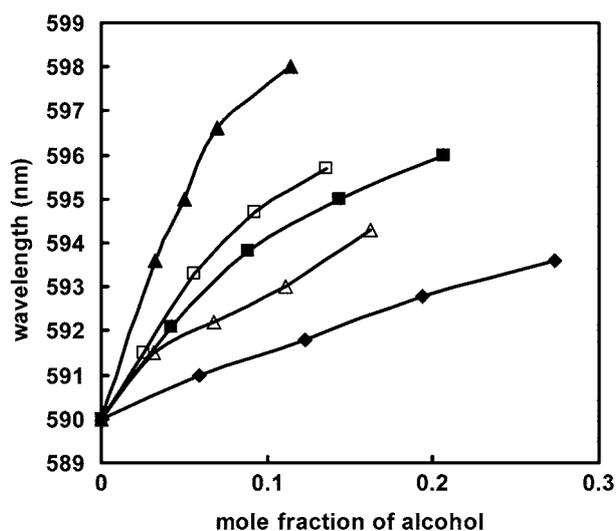


Figure 1. Variation of maximum wavelength of BPB vs. mole fraction of binary mixtures of \blacklozenge methanol, \blacksquare ethanol, \blacktriangle 1-propanol, \blacktriangledown ethylene glycol, \square 1,2-propanediol in water at room temperature.

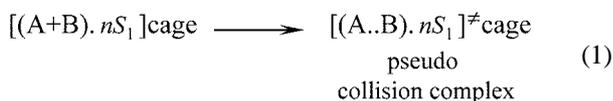
components vary, their concentration is no more constant. Also when one of solvent components acts as a reactant, the rate equations consider no distinction for it as a solvent or reactant. In the later case, in some reactions as the nonreacting solvent component concentration is increased, the reaction rate would increase as well.

Here, a new way is introduced for study of one-step chemical reactions in binary mixtures by which the role of solvent system in raising or lowering the reaction rate is inserted in the reaction rate equation. These assumptions are given by one of the authors, Babak Samiey, in a model called "study of effect of solvent mixture on the one-step reaction rates using the transition state theory and cage effect" (SESMORTAC model). In this model it is assumed that:

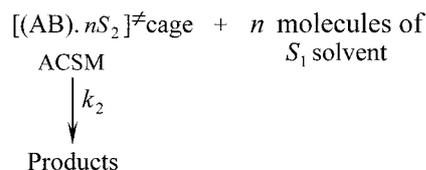
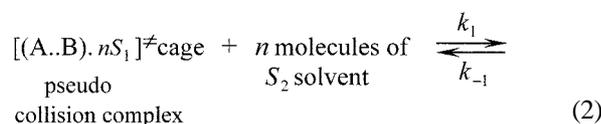
1- One-step reaction in binary mixture solution proceeds simultaneously by two parallel mechanisms. The first mechanism is similar to the reaction mechanism in pure solvent. In the second mechanism, the added solvent involves in the formation of activated complex as well. The total reaction rate is the sum of these two reactions.

2- Here for calculating the concentration of activated complex formed in the second mechanism (ACSM), it was assumed that with the beginning of the interaction between interacting species, for example A and B, we would face a chemical species (A..B), here called pseudo collision complex. These molecules can be viewed as being surrounded by a cage formed by solvent molecules. Cage effect keeps A and B molecules close together for a relatively long time, during which they collide repeatedly with each other and with the cage walls of solvent molecules.¹¹⁻¹³

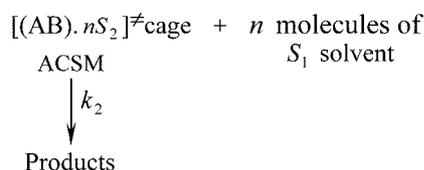
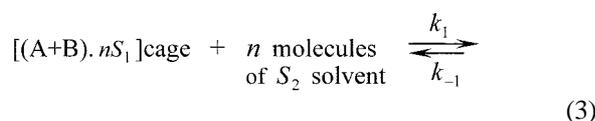
In the second mechanism, the reaction occurs in two steps. The first step is



The primary interaction would insignificantly raise the potential energy. This assumption is considered for considering the total solvent effects from the beginning of interaction between interacting species to formation of ACSM. The second step is, for example, as follows:



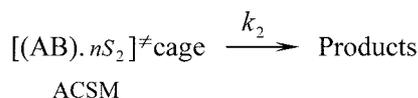
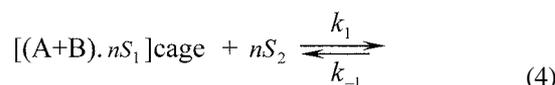
In the process of formation of ACSM from pseudo collision complex in binary mixture solutions of S_1 and S_2 solvents, the n molecules of S_1 (in the cage or solvation shell of pseudo collision complex) would be replaced by n molecules of S_2 (from bulk solution). Using the steady-state approximation for calculation of ACSM concentration, the reaction rate equation would be given upon the concentration of binary mixture components. Thus, the overall reaction equation is the sum of steps (1) and (2).



and the rate equation in binary mixture is $v = k_{\text{obs}}[A][B]$, where k_{obs} is the observed second-order rate constant in solvent mixture.

Calculations for three types of reactions are given below:

(I) Calculation of the solvent mixture effect on the reaction rate of bimolecular reaction between A and B (for example, Diles-Alder reactions) is given below. Here, the reaction rate increases with adding the S_2 solvent component.



where S_1 and S_2 are binary mixture components and k_1 , k_{-1} and k_2 are fundamental rate constants in solution. The dimension of k_1 is in $(\text{dm}^3 \text{mol}^{-1})^{n+1} (\text{time})^{-1}$ and the dimensions of k_{-1} and k_2 are in $(\text{dm}^3 \text{mol}^{-1})^n (\text{time})^{-1}$ and $(\text{time})^{-1}$.

The rate equation in pure S_1 is $v_1 = k[A][B]$ (5)

where k is the observed second-order rate constant in pure S_1 .

Assuming that a steady-state concentration is attained for ACSM,

$$[ACSM] = \frac{k_1[A][B][S_2]^n}{k_{-1}[S_1]^n + k_2} \quad (6)$$

The related rate equation, v_2 , is as follows

$$v_2 = k_2[ACSM] \quad (7)$$

substituting equation (6) for (7) we have

$$v_2 = \frac{k_2 k_1 [A][B][S_2]^n}{k_{-1}[S_1]^n + k_2} \quad (8)$$

and the equation of overall reaction rate in binary mixture is

$$v = v_1 + v_2 = k_{\text{obs}}[A][B] = \left(k + \frac{k_2 k_1 [S_2]^n}{k_{-1}[S_1]^n + k_2} \right) [A][B] \quad (9)$$

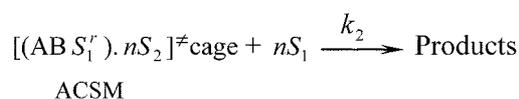
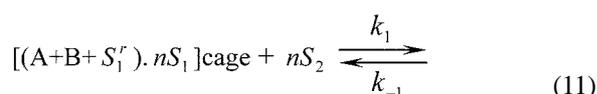
Thus the rate constant equation in binary solutions is

$$k_{\text{obs}} = k + \frac{k_2 k_1 [S_2]^n}{k_{-1}[S_1]^n + k_2} \quad (10)$$

where k_{obs} is the observed second-order rate constant in solvent mixture.

(II) Calculation of the solvent mixture effect on the rate of reaction between A, B and S_1^r , where S_1^r is the solvent molecule which reacts with A and B (for example, base hydrolysis of coordination complexes). Here, there are two cases:

IIa - By increasing the concentration of S_2 component, the reaction rate increases:



The rate equation in pure S_1 is $v_1 = k[A][B][S_1^r]$ (12)

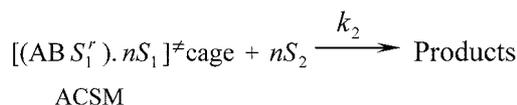
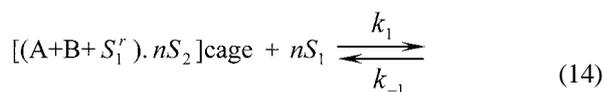
where k is the third-order rate constant in pure S_1 . Doing the calculations the rate constant equation in mixture solutions is given as:

$$k_{\text{obs}} = \left(k + \frac{k_2 k_1 [S_2]^n}{k_{-1}[S_1]^n + k_2} \right) [S_1^r] \quad (13)$$

where k_{obs} is the observed second-order rate constant in binary mixture solution. The dimension of k_1 is in $(\text{dm}^3 \text{mol}^{-1})^{n+2}(\text{time})^{-1}$ and the dimensions of k_{-1} and k_2 are in $(\text{dm}^3 \text{mol}^{-1})^n(\text{time})^{-1}$ and $(\text{time})^{-1}$.

IIb - By increasing the concentration of S_2 component, the reaction rate decreases.

It should be noted that in case IIb (and similarly in IIIb) as S_1 solvent is considered as one of reactants, the reaction rate in pure S_2 solvent is equal to zero. Because the reaction rate raises adding the S_1 solvent, thus the IIb case (and IIIb) is considered as the addition of S_1 solvent to a solvent mixture containing a certain amount of S_2 component.



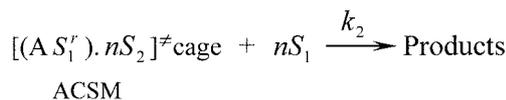
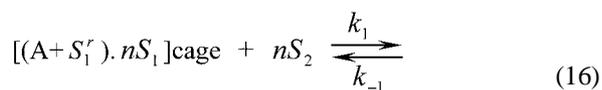
The rate equation for a solution with a given concentration of S_1 is $v_1 = k[A][B][S_1^r]$, where k is the third-order rate constant in this solution. By increasing the concentration of S_1 component, finally the equation of rate constant in mixture solutions is

$$k_{\text{obs}} = \left(k + \frac{k_2 k_1 [S_1]^n}{k_{-1}[S_2]^n + k_2} \right) [S_1^r] \quad (15)$$

where k_{obs} is the observed second-order rate constant in binary mixture solution.

(III) Calculation of the solvent mixture effect on the rate of reaction between A and S_1^r , where S_1^r is the solvent molecule which reacts with A (for example, solvolysis of coordination complexes). Here, there are also two cases:

IIIa - By increasing the concentration of S_2 component, the reaction rate increases:



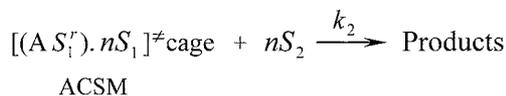
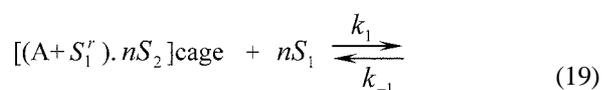
The rate equation in pure S_1 is $v_1 = k[A][S_1^r]$ (17)

where k is the second-order rate constant in pure S_1 . Finally the equation of rate constant in mixture solutions is

$$k_{\text{obs}} = \left(k + \frac{k_2 k_1 [S_2]^n}{k_{-1}[S_1]^n + k_2} \right) [S_1^r] \quad (18)$$

where k_{obs} is the observed first-order rate constant in binary mixture solution. The dimension of k_1 is in $(\text{dm}^3 \text{mol}^{-1})^{n+1}(\text{time})^{-1}$ and the dimensions of k_{-1} and k_2 are in $(\text{dm}^3 \text{mol}^{-1})^n(\text{time})^{-1}$ and $(\text{time})^{-1}$.

IIIb - By increasing the concentration of S_2 component, the reaction rate decreases:



The rate equation in a solution containing a given concentration of S_2 is $v_1 = k[A][S_1^r]$, where k is the second-order rate constant in this solution. Finally the equation of rate constant is

$$k_{\text{obs}} = \left(k + \frac{k_2 k_1 [S_1]^n}{k_{-1} [S_2]^n + k_2} \right) [S_1^r] \quad (20)$$

Where k_{obs} is the observed first-order rate constant in binary mixture solution.

3- Using the logarithm of the reaction rate constant versus the reciprocal of the dielectric constant equations, we may determine whether the reaction mechanism is changed, modifying the dielectric constant of binary mixtures due to the changes in its composition.¹⁴

Here, a range of solvent composition in which the equations of logarithm of the reaction rate constant versus the reciprocal of the dielectric constant are linear, is called "zone". A solvent composition in which a zone finishes and another zone initiates, is called "mechanism change point" (mc point). In this case, the rate constant equations in mc point are similar with equations (5), (12) and (17), where v_1 , k , $[S_1]$ and $[S_2]$ are replaced by v_{mc} , k_{mc} , $[S_1]_{mc}$ and $[S_2]_{mc}$, respectively. Then in equations (10), (13) and (18), k is replaced by k_{mc} , $[S_2]$ and $[S_1]$ are replaced by $[S_2] - [S_2]_{mc}$, $[S_2]_{mc} - [S_1]$ (because the interaction of added solvent mixture after each mc point with the species already presented in solution is not the same as before that point and it causes a change in the values of n and fundamental rate constants of reaction), respectively and we have:

$$k_{\text{obs}} = k_{mc} + \frac{k_2 k_1 ([S_2] - [S_2]_{mc})^n}{k_{-1} ([S_1]_{mc} - [S_1])^n + k_2} \quad (21)$$

$$k_{\text{obs}} = \left(k_{mc} + \frac{k_2 k_1 ([S_2] - [S_2]_{mc})^n}{k_{-1} ([S_1]_{mc} - [S_1])^n + k_2} \right) [S_1^r] \quad (22)$$

Where k_{mc} and v_{mc} are rate constant and reaction rate and $[S_1]_{mc}$ and $[S_2]_{mc}$ are concentrations of S_1 and S_2 solvent components in mc point, respectively. In equations (15) and (20), $[S_1]$ and $[S_2]$ are replaced with $[S_1] - [S_1]_{mc}$ and $[S_2]_{mc} - [S_2]$, respectively and we have:

$$k_{\text{obs}} = \left(k_{mc} + \frac{k_2 k_1 ([S_1] - [S_1]_{mc})^n}{k_{-1} ([S_2]_{mc} - [S_2])^n + k_2} \right) [S_1^r] \quad (23)$$

4- Observed reaction rate constant equations (10), (13) and (18) follow Arrhenius law. So, we may write:

$$\frac{d \ln k'}{d \left(\frac{1}{T} \right)} = -\frac{E_a}{R} = \frac{d \ln k_1}{d \left(\frac{1}{T} \right)} + \frac{d \ln \left(\frac{k_2 [S_2]^n}{k_{-1} [S_1]^n + k_2} \right)}{d \left(\frac{1}{T} \right)} \quad (24)$$

Where in equation (10) we have $k' = k_{\text{obs}} - k$ and in equations (13) and (18) we have $k' = k_{\text{obs}}/[S_1^r] - k$. As seen in the right side of equation (24) the first term shows that k_1 follows Arrhenius law while the second term shows that k_{-1}

Table 1. Rate constant values of [2+2] cycloaddition reaction between diethyl azodicarboxylate and ethyl vinyl ether in aqueous solutions of methanol (Type I) and n , k_{-1} , k_1 and k_2 values obtained from SESMORTAC model at 303 K (ref. 17)

[MeOH] (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	$k_{\text{obs}} \times 10^5$ (dm ³ mol ⁻¹ s ⁻¹)
24.71	0	36.8
22.57	5.77	58
20.1	12	153
17.9	17.2	649
15.52	22.7	1148
13	28.3	3636

* n , k_1 , k_{-1} and k_2 values for this reaction are 2.65, 1120 (dm³mol⁻¹)ⁿ⁺¹s⁻¹, 2.66×10^{-3} (dm³mol⁻¹)ⁿ s⁻¹ and 10^{-8} s⁻¹, respectively.

Table 2. Rate constant values of base hydrolysis of [(tetren)-CoO₂CCH₂NH₂]²⁺ complex in methanol-water media (Type IIa) at 293-313 K (ref. 18)

[MeOH] (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	k_{obs} (dm ³ mol ⁻¹ s ⁻¹) at			
		293 K	298 K	308 K	313 K
0	55.55	33	65	249	420
1.3	52.8	37	68	267	525
2.46	50.4	39	78	307	618
5.01	45.1	47	89	377	736
7.59	39.7	53	105	451	953
10.2	34.2	63	126	552	1140
12.8	28.7	73	148	686	1410
15.4	23.1	91	172	728	1340
17.87	17.5	96	194	817	1520
20.06	12.43	127	250	1010	1900

Table 3. n , k_{-1} , k_1 and k_2 values obtained from SESMORTAC model for base hydrolysis of [(tetren)CoO₂CCH₂NH₂]²⁺ complex in methanol-water media (Type IIa) at 293-313 K (ref. 18)

T(K)	n	$k_2 \times 10^{14}$ (dm ³ mol ⁻¹) ⁿ⁺² s ⁻¹	$k_{-1} \times 10^7$ (dm ³ mol ⁻¹) ⁿ s ⁻¹	$k_1 \times 10^{-7}$ (s ⁻¹)
293	1.25	3.658	2.39	3.39
298	1.24	10	30	31.9
308	1.143	53.6	6.9	5.64
313	1.1	76.9	2.3	2.6

*Arrhenius law of k_1 was found to be $k_1 = 6 \times 10^{29} \exp(-124494/RT)$, $r = 0.99$.

and k_2 individually do not follow Arrhenius law. Calculations similar to those above would be satisfied for equations (15), (20), (21), (22) and (23).

Some papers were analyzed with SESMORTAC model and the results were shown in Tables 1-9. Data were fitted properly in related rate constant equations by using Sigma-Plot curve fitting software. Molar concentrations of solvent mixtures components were calculated using reference.¹⁵ Dielectric constant values were obtained from the data of Akerlof.¹⁶ As seen in Tables 1, 2 and 6, for any certain temperature the reaction mechanism would not change with the changes in solvent composition, while it changes in

Table 4. Rate constant values of solvolysis of trans-Dichlorotetra(4-*t*-Butylpyridine) cobalt(III) ions in mixtures of water with methanol (Type IIIa) at 313-333 K (ref. 19)

[MeOH] (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹) at				
		313 K	318 K	323 K	328 K	333 K
1.24	52.94	0.66	1.2	2.47	4.91	10.2
2.48	50.35	0.69	1.25	2.61	5.1	10.2 ← mc_1
3.73	47.7	0.73	1.36	2.66	5.6	11
5	45.14	0.79	1.51 ← mc	2.87	6.1	11.9
7.5	39.85	0.86	1.67	3.3	7.1 ← mc	13.9
10.05	34.5	0.92	1.76	3.75 ← mc	7.8	14.4 ← mc_2
12.56	29.21	1.08 ← mc	1.99	4.03	8.4	15.8
15.06	23.8	1.14	2.26	4.39	9	16.9
17.5	18.4	1.24	2.48	4.63	9.8	18

Table 5. n , k_{-1} , k_1 and k_2 values obtained from SESMORTAC model for solvolysis of trans-Dichlorotetra(4-*t*-Butylpyridine)cobalt(III) ions in mixtures of water with methanol (Type IIIa) at 313-333 K (ref. 19)

T (K)	k_{mc} (s ⁻¹)	n	k_2 (dm ³ mol ⁻¹) ⁿ⁺¹ s ⁻¹	k_{-1} (dm ³ mol ⁻¹) ⁿ s ⁻¹	$k_1 \times 10^8$ (s ⁻¹)
313(2nd zone)	0.66×10^{-4}	1.59	4.97	1.78×10^{-8}	302
313(3rd zone)	1.08×10^{-4}		Data are not sufficient		
318(2nd zone)	1.2×10^{-4}		Data are not sufficient		
318 (3rd zone)	1.51×10^{-4}	2.05	5.64	2.98×10^{-9}	660
323(2nd zone)	2.47×10^{-4}	1.5	23.3	7.9×10^{-9}	380
323 (3rd zone)	3.75×10^{-4}		Data are not sufficient		
328 (2nd zone)	4.91×10^{-4}	2.47	20.8	0.58	260
328 (3rd zone)	7.1×10^{-4}	1.73	63.8	4×10^{-10}	26
333 (2nd zone)	10.2×10^{-4}	1.437	194	11.7	903
333 (3rd zone)	14.4×10^{-4}		Data are not sufficient		

Table 6. Rate constant values of base hydrolysis of ($\alpha\beta$ S)-(o-Methoxy benzoato) (tetraethylenepentamine)-cobalt(III) in methanol-water media (Type IIa) at 293-313 K (ref. 20)

[MeOH] (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	k_{obs} (dm ³ mol ⁻¹ s ⁻¹) at			
		293 K	298 K	308 K	313 K
1.3	52.8	56	108	393	676
2.46	50.4	60	117	425	749
5.01	45.1	67	134	489	958
7.59	39.7	75	159	632	1177
10.2	34.2	87	188	814	1495
12.8	28.7	105	230	1000	1903
15.4	23.1	136	301	1295	1769
17.87	17.5	188	386	1733	3618

Table 7. n , k_{-1} , k_1 and k_2 values obtained from SESMORTAC model for base hydrolysis of ($\alpha\beta$ S)-(o-Methoxy benzoato) (tetraethylenepentamine)cobalt(III) in methanol-water media (Type IIa) at 293-313 K (ref. 20)

T (K)	n	k_2 (dm ³ mol ⁻¹) ⁿ⁺² s ⁻¹	k_{-1} (dm ³ mol ⁻¹) ⁿ s ⁻¹	k_1 (s ⁻¹)
293	3.52	4.84×10^{-4}	6×10^{-12}	1054
298	3.127	3×10^{-3}	7.2×10^{-12}	333
308	3.15	1.27×10^{-2}	6.33×10^{-16}	0.017
313	3.01	4.19×10^{-2}	2.7×10^{-15}	0.07

*Arrhenius law of k_1 was found to be $k_1 = 3 \times 10^{26} \exp(-166496/RT)$, $r = 0.989$.

Table 8. Rate constant values of solvolysis of chloropentakis (methylamine) cobalt(III) ion in mixtures of water with methanol (Type IIIb) at 308-318 K (ref. 21)

[MeOH] (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹) at		
		308 K	313 K	318 K
0	55.55	1.2	2.1	3.85
1.544	52.23	0.962	1.76	3.62 ← mc_1
3.064	49.08	0.8	1.68 ← mc_1	2.76
4.56	46	0.7	1.42	2.51
6.034	42.96	0.536	1.1	2.02
7.48	39.96	0.445	0.861	1.56
8.61	37.06	0.375 ← mc	0.7 ← mc_2	1.32 ← mc_2
11.67	31.15	0.293	0.538	1.07

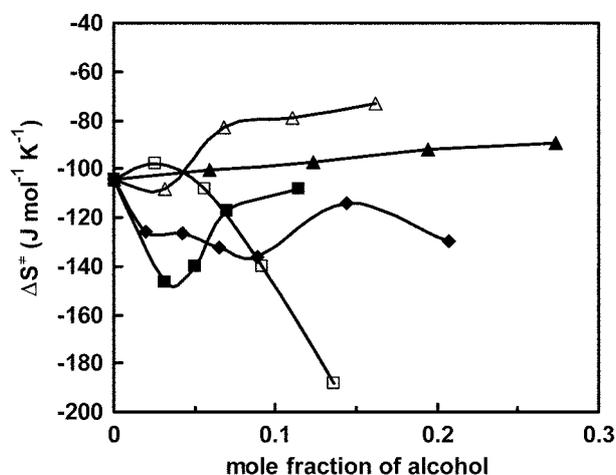
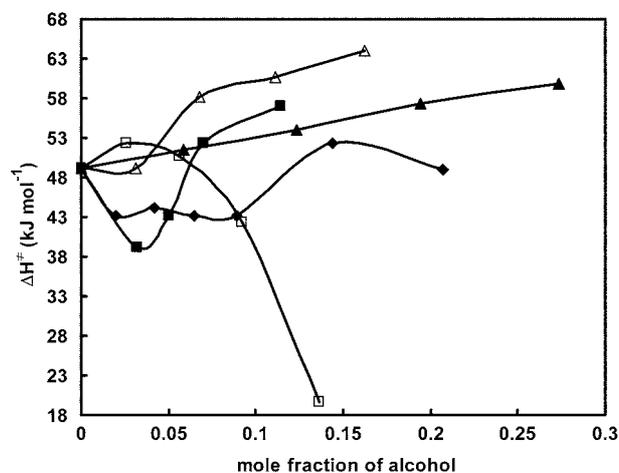
Tables 4 and 8. In zones with sufficient data the values of n , k_1 , k_{-1} and k_2 were calculated.

Results and Discussion

The rate of fading of BPB is first-order in dye and first-order in hydroxide ion.⁷ Since the concentration of NaOH solution was far greater than the dye, the reaction was pseudo-first-order in dye. It is seen from Tables 10-15 that in all systems the k values are decreasing with the progressive addition of alcohols in the whole range of the composition.

Table 9. n , k_{-1} , k_1 and values obtained from SESMORTAC model for solvolysis of chloropentakis(methylamine)cobalt(III) ion in mixtures of water with methanol (Type IIIb) at 308-318 K (ref. 21)

T (K)	k_{mc} (s^{-1})	n	k_{-1} ($dm^3 mol^{-1} s^{-1}$) ^{$n+1$}	k_1 ($dm^3 mol^{-1} s^{-1}$) ^{n}	k_2 (s^{-1})
308(1st zone)	-	1.28	2.67×10^{-8}	9×10^{-9}	203.5
308(2nd zone)	3.75×10^{-5}		Data are not sufficient		
313(1st zone)	-		Data are not sufficient		
313(2nd zone)	1.68×10^{-4}	1.88	3.25×10^{-8}	4.6	91
313(3rd zone)	7×10^{-5}		Data are not sufficient		
318(1st zone)	-		Data are not sufficient		
318(2nd zone)	3.62×10^{-4}	1.2	1.23×10^{-7}	3.15×10^{-8}	310
318(3rd zone)	1.32×10^{-4}		Data are not sufficient		

**Figure 2.** Variation of ΔS^\ddagger values of BPB fading reaction vs. mole fraction of binary mixtures of \blacktriangle methanol, \blacklozenge ethanol, \blacksquare 1-propanol, \triangle ethylene glycol, \square 1,2-propanediol in water at room temperature.**Figure 3.** Variation of ΔH^\ddagger values of BPB fading reaction vs. mole fraction of binary mixtures of \blacktriangle methanol, \blacklozenge ethanol, \blacksquare 1-propanol, \triangle ethylene glycol, \square 1,2-propanediol in water at room temperature.

This behavior indicates that changes in internal structure of the medium on addition of solvent²²⁻²⁶ do not reflect on the reaction rates. The thermodynamic activation parameters are given in Figures 2 and 3. As seen in Figure 2, the highly negative ΔS^\ddagger values support the formation of highly restricted transition states. The observation of extrema can

be visualized in the light of change of water structure in the presence of the alcohols.²²⁻²⁶ 1,2-Diols are more associated than the monohydric alcohols. The presence of the second OH group in the molecule results in an increase of the average number of hydrogen bonds per molecule. Since the degree of hydrogen bonding varies with temperature, the

Table 10. Rate constant equations of BPB fading in methanol-water solutions obtained from SESMORTAC model at 298-308 K

$W_{MeOH}\%$	[MeOH] ($mol\ dm^{-3}$)	[H ₂ O]	$k_{obs} \times 10^2$ ($dm^3 mol^{-1} min^{-1}$) at			Rate constant equation
			298 K	303 K	308 K	
0	0	55.55	5.71 ± 0.06	7.79 ± 0.08	10.6 ± 0.1	at 298 K :
10	3.065	49.13	3.41 ± 0.05	4.65 ± 0.04	6.43 ± 0.07	$k_{obs} = \frac{178.4[H_2O]^{1.73}}{1.62 \times 10^5 [MeOH]^{1.73} + 3.3 \times 10^6}$
20	6.045	42.92	1.78 ± 0.06	2.54 ± 0.07	3.51 ± 0.08	at 303 K :
30	8.93	36.9	0.867 ± 0.12	1.24 ± 0.07	1.79 ± 0.05	$k_{obs} = \frac{439[H_2O]^{1.69}}{2.57 \times 10^5 [MeOH]^{1.69} + 5 \times 10^6}$
40	11.7	31.05	0.432 ± 0.1	0.595 ± 0.08	0.919 ± 0.12	at 308 K :
						$k_{obs} = \frac{1100[H_2O]^{1.66}}{4.2 \times 10^5 [MeOH]^{1.66} + 8.2 \times 10^6}$

Table 11. Rate constant equations of BPB fading in ethylene glycol-water solutions obtained from SESMORTAC model at 298-308 K

W _{eg} %	[eg]	[H ₂ O]	$k_{\text{obs}} \times 10^2$ (dm ³ mol ⁻¹ min ⁻¹) at			Rate constant equation
	(mol dm ⁻³)		303 K	308 K	313 K	
0	0	55.55	7.79 ± 0.08	10.6 ± 0.1	14.3 ± 0.2	at 303 K :
10	1.628	50.54	4.65 ± 0.05	6.49 ± 0.07	8.7 ± 0.08	$k_{\text{obs}} = \frac{2600[H_2O]^{1.364}}{1.92 \times 10^6[eg]^{1.364} + 8 \times 10^6}$
20	3.3	45.52	2.7 ± 0.07	3.95 ± 0.11	5.62 ± 0.08	at 308 K :
30	5.01	40.36	1.62 ± 0.1	2.43 ± 0.08	3.46 ± 0.06	$k_{\text{obs}} = \frac{4137[H_2O]^{1.325}}{1.8 \times 10^6[eg]^{1.325} + 8 \times 10^6}$
40	6.776	35.05	0.919 ± 0.12	1.4 ± 0.15	2.05 ± 0.11	at 313 K :
						$k_{\text{obs}} = \frac{11550[H_2O]^{1.264}}{3 \times 10^6[eg]^{1.264} + 1.3 \times 10^7}$

Table 12. Rate constant equations of BPB fading in 1,2-propanediol-water solutions obtained from SESMORTAC model at 303-313 K

W _{prd} %	[prd]	[H ₂ O]	$k_{\text{obs}} \times 10^2$ (dm ³ mol ⁻¹ min ⁻¹) at			Rate constant equation
	(mol dm ⁻³)		303 K	308 K	313 K	
0	0	55.55	7.79 ± 0.08	10.6 ± 0.1	14.3 ± 0.2	at 303 K :
10	1.461	50.19	4.47 ± 0.09	6.45 ± 0.1	8.7 ± 0.12	$k_{\text{obs}} = \frac{4400[H_2O]^{1.252}}{2.9 \times 10^6[prd]^{1.252} + 8.6 \times 10^6}$
20	2.947	44.8	2.57 ± 0.11	3.66 ± 0.08	4.91 ± 0.15	at 308 K :
30	4.453	39.38	1.54 ± 0.12	1.95 ± 0.07	2.64 ± 0.1	$k_{\text{obs}} = \frac{2414[H_2O]^{1.488}}{2.07 \times 10^6[prd]^{1.488} + 9 \times 10^6}$
40	5.98	33.91	1.07 ± 0.14	1.2 ± 0.11	1.4 ± 0.16	at 313 K :
						$k_{\text{obs}} = \frac{3625[H_2O]^{1.533}}{2.64 \times 10^6[prd]^{1.533} + 1.2 \times 10^7}$

Table 13. Rate constant equations of BPB fading in ethanol-water solutions obtained from SESMORTAC model at 308-318 K

W _{EtOH} %	[EtOH]	[H ₂ O]	$k_{\text{obs}} \times 10^2$ (dm ³ mol ⁻¹ min ⁻¹) at			Rate constant equation
	(mol dm ⁻³)		308 K	313 K	318 K	
0	0	55.55	10.6 ± 0.1	14.3 ± 0.2	19.4 ± 0.18	at 308 K :
5	1.074	52.21	7.98 ± 0.1	10.4 ± 0.18	13.8 ± 0.16	$k_{\text{obs}} = \frac{1590[H_2O]^{1.77}}{2.76 \times 10^6[EtOH]^{1.77} + 1.85 \times 10^7}$
10	2.131	49.1	5.4 ± 0.08	7.19 ± 0.08	9.46 ± 0.14	at 313 K :
15	3.19	46.05	3.67 ± 0.12	4.92 ± 0.12	6.32 ± 0.11	$k_{\text{obs}} = \frac{4105[H_2O]^{1.67}}{4.22 \times 10^6[EtOH]^{1.67} + 2.38 \times 10^7}$
20	4.205	43.053	2.27 ± 0.14	3.03 ± 0.13	3.94 ± 0.09	at 318 K :
30	6.212	37.1	0.919 ± 0.22	1.3 ± 0.2	1.78 ± 0.16	$k_{\text{obs}} = \frac{7.43 \times 10^5[H_2O]^{1.47}}{3.77 \times 10^8[EtOH]^{1.47} + 1.4 \times 10^9}$
40	8.12	31.17	0.53 ± 0.18	0.74 ± 0.25	0.919 ± 0.2	

liquid structure of the 1,2-diols may change considerably. Whatever the structure of the polymeric species in 1,2-propanediol, the steric effect of the CH₃- group is such that the number of possible configurations of the associated molecules is smaller than for ethylene glycol. This results in

an increased negative entropy of formation accompanying a more restricted number of configurations and makes these polymeric species more susceptible to thermal depolymerization,^{23,24} Figure 2. If ΔH^\ddagger is split into a reaction and a solvation component,²⁷ it is reasonable to expect that solvent

Table 14. Rate constant equations of BPB fading in 1-propanol-water solutions obtained from SESMORTAC model at 313-323 K

W _{PrOH} %	[PrOH]	[H ₂ O]	$k_{\text{obs}} \times 10^2$ (dm ³ mol ⁻¹ min ⁻¹) at			Rate constant equation
	(mol dm ⁻³)		313 K	318 K	323 K	
0	0	55.55	14.3 ± 0.2	19.4 ± 0.18	25.4 ± 0.23	at 313 K :
10	1.635	49.145	4.22 ± 0.11	5.46 ± 0.12	6.97 ± 0.18	$k_{\text{obs}} = \frac{0.32[H_2O]^{2.42}}{1.717 \times 10^4 [PrOH]^{2.42} + 3.71 \times 10^4}$
15	2.437	46.11	1.84 ± 0.14	2.38 ± 0.13	3.19 ± 0.14	at 318 K :
20	3.223	43.05	0.811 ± 0.15	1.14 ± 0.13	1.57 ± 0.16	$k_{\text{obs}} = \frac{0.59[H_2O]^{2.3}}{1.714 \times 10^4 [PrOH]^{2.3} + 3.15 \times 10^4}$
30	4.737	36.92	0.43 ± 0.23	0.64 ± 0.2	0.865 ± 0.18	at 323 K :
						$k_{\text{obs}} = \frac{0.71[H_2O]^{2.177}}{1.08 \times 10^4 [PrOH]^{2.177} + 1.75 \times 10^4}$

structural perturbations causing hydrogen-bond formation or breakage will affect the solvation component of ΔH^\ddagger , as this effect in the bulk phase will be passed on to the reaction site via the solvation shells of the transition and initial states.²⁰

By comparison of the rate constants in Tables 10-15, we can see at the same mole fractions and temperatures, the following relation holds for:

$$k_w > k_{\text{MeOH}} > k_{\text{eg}} > k_{\text{EtOH}} > k_{\text{prd}} > k_{\text{PrOH}} \quad (25)$$

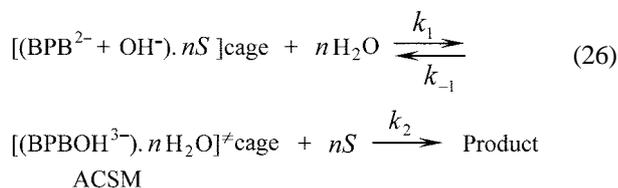
where k_w , k_{MeOH} , k_{eg} , k_{EtOH} , k_{prd} and k_{PrOH} are second-order rate constants of the BPB fading in water and in aqueous mixtures of methanol, ethylene glycol, ethanol, 1,2-propanediol and 1-propanol, respectively. This trend is opposite to the order of variation of the λ_{max} values of fading reaction in these alcohols, Figure 1. The red shift has been previously reported for other compounds upon going from polar to apolar solvents.²⁸

Proposed Reaction Mechanism. The effect of dielectric constant on the fading of BPB was studied by using the correlation of logarithm of reaction rate constant versus reciprocal of the dielectric constants of alcohol-water solutions whose values were obtained from the data of Verbeek²⁴ and Akerlof.¹⁶

This correlation in all alcohol-water mixtures was linear. So the reaction mechanism would not change in the concentration range of the used alcohol-water.

The following mechanism is proposed upon SESMORTAC model which accounts for dependence of the reaction rate of BPB fading to both water and alcohol concentrations. Due to SESMORTAC model this reaction is of type I.

NaOH does not dissolve in pure alcohol thus the reaction rate in pure alcohol is equal to zero. As adding water to solvent mixture would increase the reaction rate, mechanism of BPB fading may be outlined in the form:



where alcohol molecules are shown by S and k_1 , k_{-1} and k_2 are fundamental rate constants of BPB fading reaction in aqueous alcohol solutions. Assuming that a steady-state concentration of ACSM is attained in the mixed solvent, we have:

$$[ACSM] = \frac{k_1 [BPB^{2-}] [OH^-] [H_2O]^n}{k_{-1} [S]^n + k_2} \quad (27)$$

and the rate equation is

$$v = k_2 [ACSM] \quad (28)$$

by substituting (27) for (28) we have:

$$v = \frac{k_2 k_1 [BPB^{2-}] [OH^-] [H_2O]^n}{k_{-1} [S]^n + k_2} \quad (29)$$

thus the rate changes directly with $[H_2O]^n$ and inversely with $[S]^n$.

The experimental rate equation of BPB fading is:

$$v = k_{\text{obs}} [BPB^{2-}] [OH^-] \quad (30)$$

where k_{obs} is the observed second-order rate constant in alcohol-water mixture.

By equating (29) and (30) we have :

$$k_{\text{obs}} = \frac{k_2 k_1 [H_2O]^n}{k_{-1} [S]^n + k_2} \quad (31)$$

The reaction rate is lowered severely in solvent mixtures with high alcohol concentration. By assuming that reaction mechanism would not change in the full concentration range of the used alcohol-water systems (0-100% weight percent of alcohol), the data of Tables 10-15 properly fitted in equation (31) and k_1 , k_{-1} , k_2 and n values in different alcohol-water solvent systems were given in Table 15. Molar concentrations of water and alcohols of alcohol-water systems in this work have been derived from references.^{15,24}

Using SESMORTAC model, it is observed that in any solvent system except 1,2-propanediol-water system, as it is

Table 15. n , k_1 , k_{-1} , k_2 and values for BPB fading in various alcohol-water media obtained from SESMORTAC model at different temperatures

T(K)	n	k_1 ($\text{dm}^3\text{mol}^{-1}$) ^{$n+1$} min^{-1}	k_{-1} ($\text{dm}^3\text{mol}^{-1}$) ^{n} min^{-1}	k_2 (min^{-1})	$E_a(k_1)$ (kJ mol^{-1})
Methanol + water					
298	1.73	5.41×10^{-5}	1.62×10^5	3.3×10^6	
303	1.69	8.78×10^{-5}	2.57×10^5	5×10^6	75.5
308	1.66	1.34×10^{-4}	4.2×10^5	8.2×10^6	
Ethylene glycol + water					
303	1.364	3.25×10^{-4}	1.92×10^6	8×10^6	
308	1.325	5.17×10^{-4}	1.8×10^6	8×10^6	83.6
313	1.264	8.88×10^{-4}	3×10^6	1.3×10^7	
1,2-Propanediol + water					
303	1.252	5.12×10^{-4}	2.9×10^6	8.6×10^6	
308	1.488	2.68×10^{-4}	2.07×10^6	9×10^6	–
313	1.533	3.02×10^{-4}	2.64×10^6	1.2×10^7	
Ethanol + water					
308	1.77	8.6×10^{-5}	2.76×10^6	1.85×10^7	
313	1.67	1.72×10^{-4}	4.22×10^6	2.38×10^7	151.5
318	1.47	5.31×10^{-4}	3.77×10^8	1.4×10^9	
1-Propanol + water					
313	2.42	8.62×10^{-6}	1.717×10^4	3.71×10^4	
318	2.3	1.87×10^{-5}	1.714×10^4	3.15×10^4	129.0
323	2.177	4.06×10^{-5}	1.08×10^4	1.75×10^4	

* $E_a(k_1)$ values were obtained from Arrhenius law of k_1 .

seen from Table 15, with temperature raise the k_1 values are increased and n values are decreased. At each temperature the fundamental rate constant values change as follows:

$$k_2 > k_{-1} \gg k_1 \quad (32)$$

Relation (32) shows that the formation of activated complex from reactants is the rate-determining step.

From Table 15, we see that in the same temperature the order of n value changes in alcohol-water solvents are:

$$\text{Ethylene glycol} < \text{Methanol} < \text{Ethanol} < \text{1-Propanol} \quad (33)$$

From Table 15, we see that in the same temperature the order of k_1 value changes in alcohol-water solvents are:

$$\text{1-Propanol} < \text{Ethanol} < \text{Methanol} < \text{Ethylene glycol} \quad (34)$$

The α (hydrogen bond donor acidity) and π^* (depolarity/polarizability) solvatochromic parameters of pure alcohols^{29,31} vary the same way as the relation (34), which is reciprocal of the order of n value changes. This may be resulted from one sulfonate and two phenoxide groups bound with activated complex.

As mentioned earlier, it seems that the reason for disordered changes of the n and k_1 values of 1,2-propanediol-water system (in Table 15) results from thermal depolymerization of polymeric species of 1,2-propanediol in the solution that increases the n values of BPB fading in aqueous 1,2-propanediol solutions with increase in temperature.

Summary

We have studied the effect of a number of binary alcohol-water mixtures on the rate of BPB fading reaction using SESMORTAC model. We deduced the fundamental rate constants of this reaction in these mixtures and it was observed that the formation of activated complex from reactants is the rate-determining step. We believe that the data reported here provide new insights into the study of the effect of binary mixture solvents on the rate of one-step reactions.

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